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B411 B729**

(56) Documents Cited

**GB 0781803 A WO 99/64638 A1 WO 98/49371 A1  
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Scandinavica, Vol 45, 1991, pages 145-157**

(58) Field of Search

**UK CL (Edition S ) C7B BCBX BDCA BDCC BDCF BDCJ  
BDCK BDCN BDDA BDDB BDDC BEDL  
INT CL<sup>7</sup> C22B 21/00 21/02 21/04 34/12 , C25C 3/26  
3/28 , C25F 1/12 1/16  
Online: WPI, EPODOC, JAPIO**

(54) Abstract Title

**Electrolytic reduction of metal oxides**

(57) A method of removing oxygen from a solid metal, metal compound or semi-metal  $M_1O$  eg  $TiO_2$  by electrolysis in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that reaction of X rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$  and wherein,  $M_1O$  is in the form of a granules or is in the form of a powder which is continuously fed into the fused salt, thereby producing titanium.

Also disclosed is a method of producing a metal foam comprising the steps of fabricating a foam-like metal oxide preform, removing oxygen from said foam structured metal oxide preform by electrolysis in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that reaction of oxygen rather than  $M_2$  deposition occurs at an electrode surface.

In further modifications metal matrix composites and fibre reinforced metal matrix composites are produced using this technique. In addition when titanium powder is being produced from  $TiO_2$  a second cathode may be provided maintained at a potential which is more negative than the first cathode so that dendritic titanium is deposited thereon. In a yet further modification a ceramic facsimile of the component formed from titanium oxide or a mixture of titanium dioxide and oxides of appropriate alloying elements may be used.

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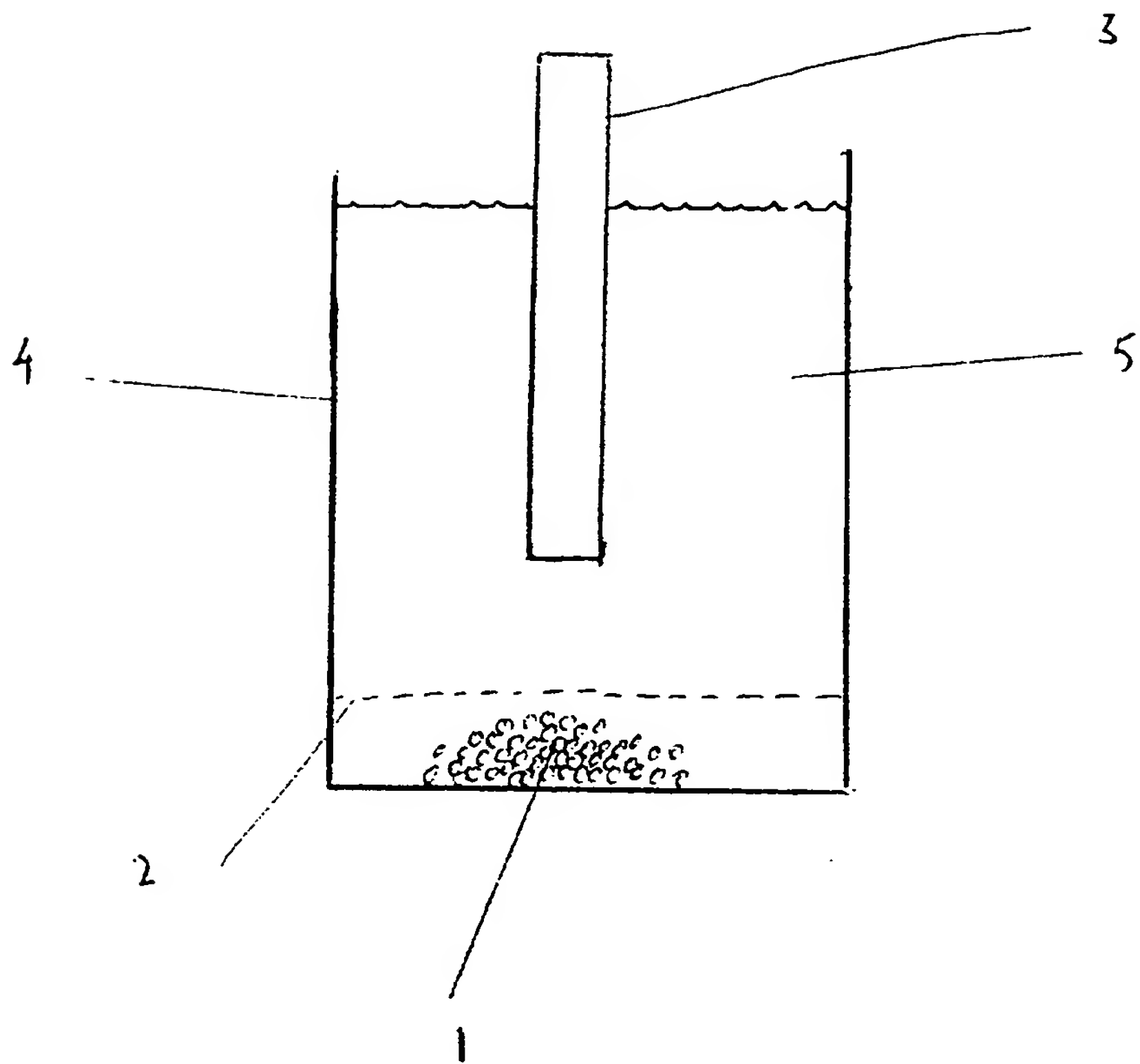


FIG 1

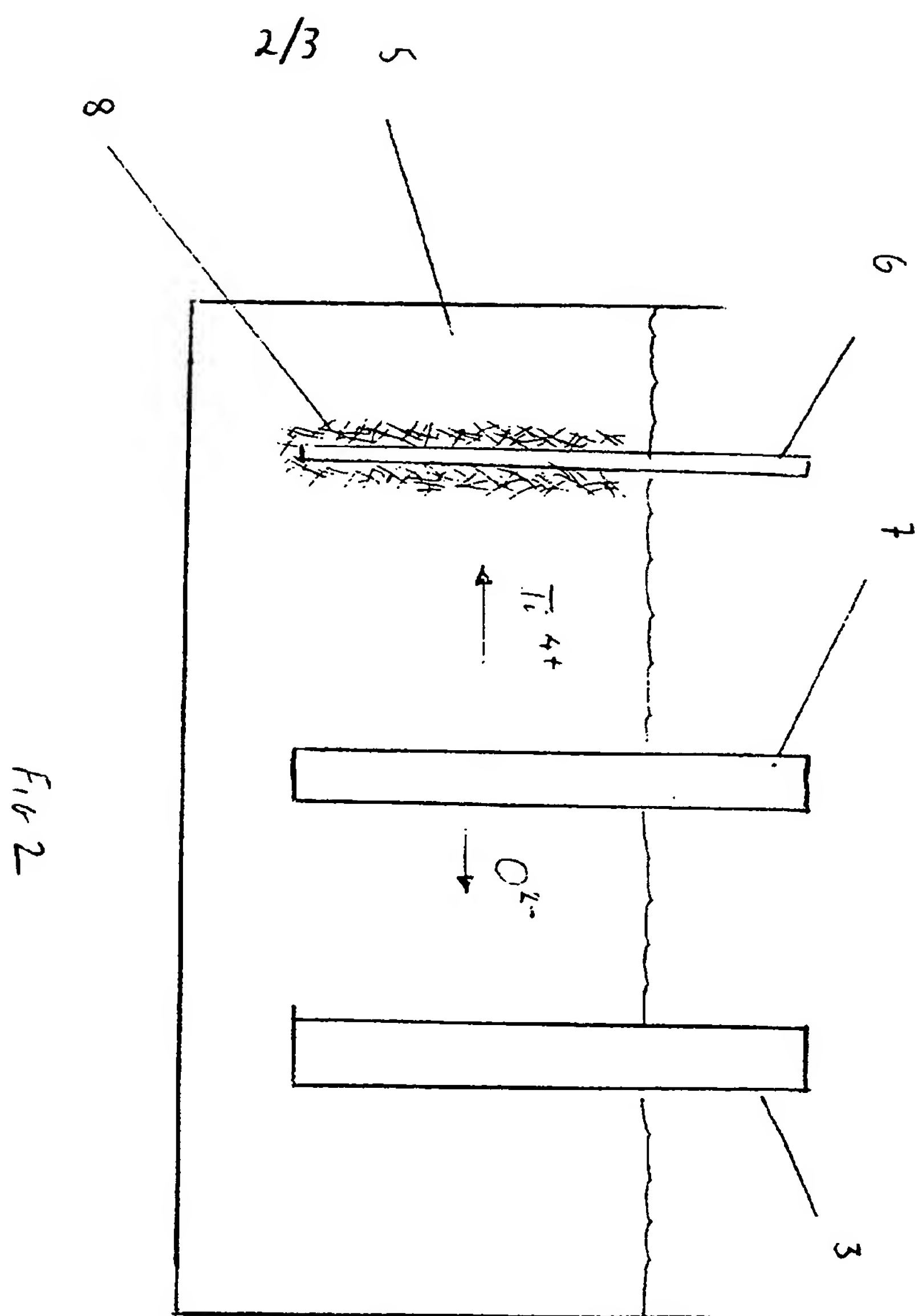


Fig 2

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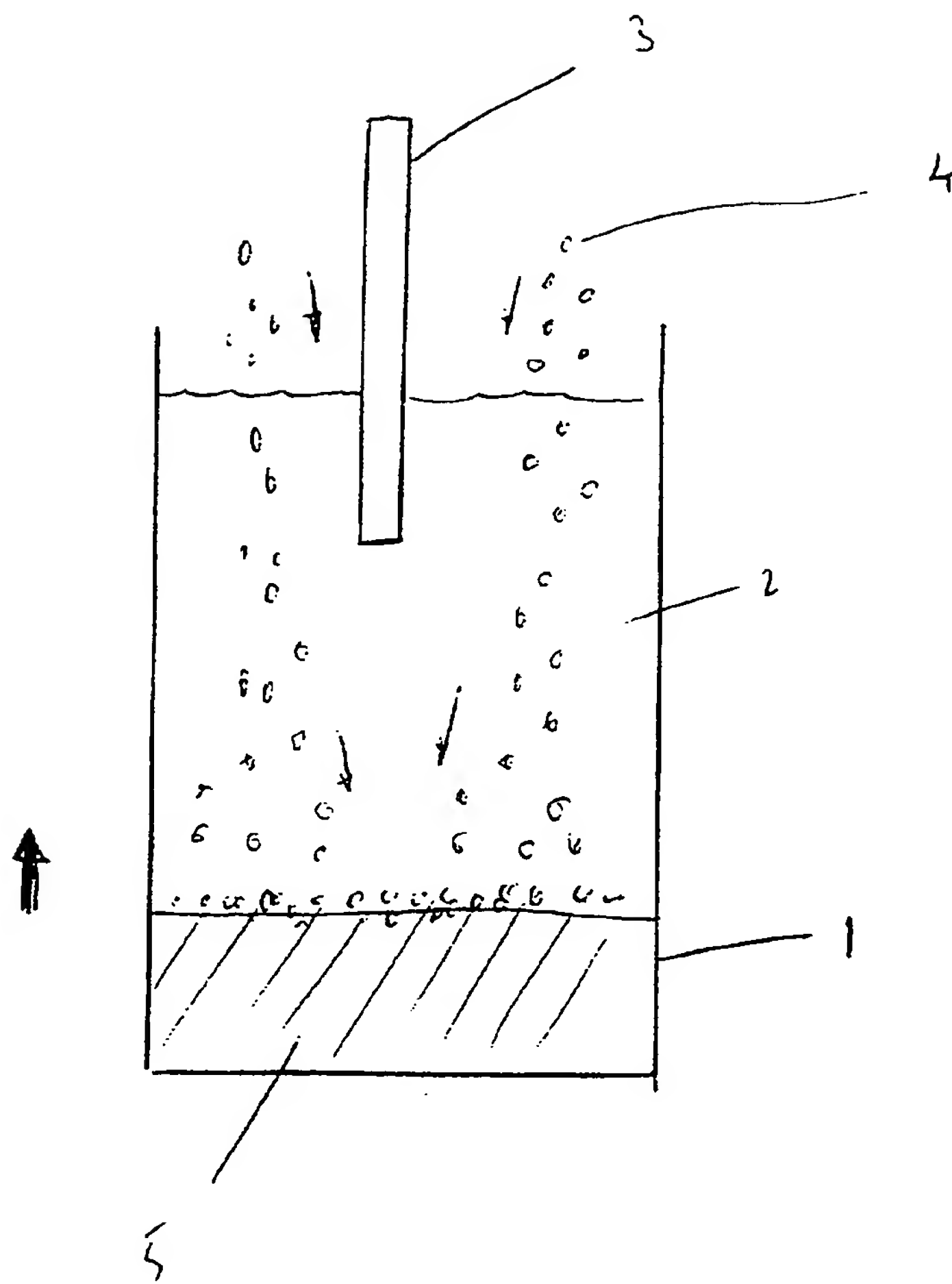


Fig 3

### Improvements in the electrolytic reduction of metal oxides

The invention relates to improvements in the electrolytic reduction in metal compounds and in particular to improvements in the reduction of titanium oxide to produce metallic titanium.

International Patent Specification PCT/GB99/01781 describes a method of the removal of oxygen from metals and metal oxides. The method involves the electrolysis of the oxide in a fused salt, and wherein the electrolysis is performed under conditions such that the reaction of oxygen rather than the cation of the salt deposition occurs at an electrode surface and such that oxygen dissolves in the electrolyte. The metal or metal oxide to be reduced is made the cathode.

The current inventors have developed improvements to this process which greatly enhance the efficiency and usefulness of the general technique.

The invention will now be described by way of examples only and with reference to the following figures of which:

Figure 1 shows an embodiment wherein the metal oxide to be reduced is in the form of granules.

Figure 2 shows an embodiment wherein an additional cathode is provided in order to refine the metal to the dendritic form.

Figure 3 shows an embodiment showing the use of continuous powder feed.

#### Production of powder by reduction of sintered metal oxide granules

The inventors have determined that sintered granules or powder of metal dioxide can be used as the feedstock for the electrolysis used in the above referenced method, as long as appropriate conditions are present. This has the advantage that it would allow very efficient and direct production of

titanium metal powder, which is at present very expensive. In this method, powdered titanium dioxide in the form of granules or a powder preferably have a size in the region of 200  $\mu\text{m}$  diameter.

In an example illustrated by figure 1, the granules of titanium dioxide 1 are held in a basket 2 below a carbon anode 3 located in a crucible 4 having a molten salt 5 therein. These are prevented from sintering together by maintaining particle motion by any appropriate method e.g. in a fluidised bed arrangement. Agitation is provided either by mechanical vibration or by the injection of gas underneath the basket. Mechanical vibration can for example be in the form of ultrasonic transducers mounted on the outside of the crucible or on control rods. The key variables to adjust are the frequency and amplitude of the vibrations in order to get an average particle contact time which is long enough to get reduction, but short enough to prevent diffusion bonding of the particles into a solid mass. Similar principles would apply to the agitation by gas, except here the flow rate of gas and size of the bubbles would be the variables controlling particle contact time. Additional advantages of using this technique are that the batch of powder reduces evenly, and, due to the small size of the particles, rapidly. Also the agitation of the electrolyte helps to improve the reaction rate.

In the above example, titanium is obtained by the method from titanium oxide. However the method can be applied to most metal oxides to produce the metal.

#### Production of powder by deposition of Ti onto the cathode

The inventor has determined that if titanium is deposited onto a cathode (based on the electrolytic process stated above) from another source of titanium at a more positive potential, the resulting titanium deposited thereon is dendritic in structure. This form of titanium is easy to break up into a powder since individual particles of titanium are connected together by only a small area.

This effect can be used for producing titanium powder from titania. In this refinement, shown in Figure 2, of the above referenced method, a second cathode 6 is provided which is maintained at a potential which is more negative than the first cathode 7. When the deposition of titanium on the first cathode has progressed sufficiently, the second electrode is switched on, leading to the dissolution of titanium from the first cathode and deposition onto the second cathode, in dendritic form 8. The other reference numerals represent the same items as in figure 1.

The advantage of this process is that dendritic deposited titanium is easily turned into powder. This process will also add an additional refining step in the reduction of titania which should result in a higher product purity.

#### Feedstock production by addition of binder to rutile and amorphous titania

The manufacture of titanium dioxide from the raw ore (sand mined illemite) comprises a large number of steps in the production of titanium.

During one of these stages titanium oxide in the form of amorphous slurry undergoes calcining. The inventors have determined that the titanium dioxide slurry can be used as the principle feedstock for titanium production and has the advantage that it is cheaper to produce. However it has been found that the amorphous  $\text{TiO}_2$  does not sinter very well; it tends to crack and disintegrate even when mixed with a binder beforehand. This occurs because of the fine particle size of the amorphous material which prevents close packing of the powder before sintering. The result of this is large shrinkage during the sintering process which resulted in a disintegrated as-sintered product. However it has been determined that if a small percentage of the more expensive calcined material is mixed with the amorphous material and a binder satisfactory results after sintering are obtained. This quantity should be at least 5% of the calcined material.

#### Production of alloy metal matrix composites (MMC's)

The manufacture of metal or alloy MMC reinforced with ceramic fibres or particles is known to be difficult and expensive. For fibre reinforced MMC's, existing methods all use solid state diffusion bonding to produce a 100% dense composite and differ only in the way the metal and fibre is combined prior to hot pressing. Current methods introduce the metal in the form of foil, wire, or powder, or by plasma spray droplets onto arrays of fibres, or by vapour coating of individual fibres with metal/alloy.

The inventor have determined that in order to produce a fibre reinforced MMC, individual SiC fibres can be coated with an oxide/binder slurry (or mixed oxide slurry for an alloy) of the appropriate thickness, or the fibres can be combined with oxide paste or slurry to produce a preformed sheet consisting of parallel fibres in a matrix of oxide powder and binder or a complex three dimensional

shape containing the silicon fibres in the correct positions could be cast or pressed from oxide slurry or paste. The coated fibre, preform sheet or three dimensional shape can then be made the anode of an electrolytic cell (with or without a pre-sinter step) and the oxide powder would be reduced by the electrolytic process mentioned above to a metal or alloy. The product can then be washed or vacuum annealed to remove the salt and then hot isostatically pressed to give a 100% dense fibre reinforced composite.

For a particulate reinforced titanium alloy MMC, the preferred traditional production route is by mixing of powders and hot pressing. Liquid phase processing is not normally favourable, because of problems with the size and distribution of phases formed from the liquid phase. However, it is also difficult to achieve an even distribution of ceramic particles by blending of metal and ceramic powders, particularly when the powders are of different size ranges, which is invariably the case with titanium powder. In the proposed method, fine ceramic particles such as titanium diboride are blended with titania powder to give a uniform mixture prior to sintering and electrolytic reduction. After reduction the product is washed or vacuum annealed to remove salt, and then hot pressed to give a 100% dense composite material. Depending on the reaction chemistries, the ceramic particles either remain unchanged by the electrolysis and hot pressing or would be converted to another ceramic material which would then be the reinforcement. For example, on the case of titanium diboride, the ceramic reacts with the titanium to form titanium monoboride. In a variation of the new process, fine metal powder is mixed with the titania powder in place of a ceramic powder, with the intention of forming a fine distribution of a hard ceramic or intermetallic phase by reaction with titanium or another alloying element or elements. For example, boron powder can be added, and this reacts to form titanium monoboride particles in the alloy.

#### Use of continuous powder feed

One improvement in the electrolytic process that has been developed by the inventor is of continuously feeding a fine powder of the metal oxide. This allows for a constant current and higher reaction rate. A carbon electrode is preferred for this. Additionally cheaper feedstock can be used because a sintering and/or forming stage can be missed out.

This method is shown in figure 3 which shows a conducting crucible 1 which is made the cathode containing a molten salt 2 and inserted therein is an anode 3. Titanium dioxide powder 4 is fed into



the crucible where it undergoes reduction and is deposited at the base of the crucible. The thick arrow shows the increasing thickness of the reduced feedstock 5.

#### Production of titanium foam

Titanium foams are attractive for a number of applications such as filters, medical implants and structural fillers. Until now however, no reliable method has been found for their manufacture. Partially sintered alloy powder is similar to a foam but is expensive to produce due to the high cost of titanium alloy powder, and the porosity that can be achieved is limited to about 40%.

The inventors have determined that if one fabricates a sponge-like sintered oxide pre-form this can be converted into a solid metal/alloy foam by using the electrolysis method above. Various established methods could be used to produce a foam like material from the mixture of oxide powders. It is a requirement that the foam preform must have open porosity i.e. interconnected and open to the exterior.

In a preferred embodiment, a natural or synthetic polymeric foam is infiltrated with metal (e.g. titanium) oxide slip, dried and fired to remove the organic foam, leaving an open 'foam' which is an inverse of the original organic foam. The sintered preform is then electrolytically reduced to convert it into a titanium/titanium alloy foam. This is then washed or vacuum distilled to remove the salt.

In an alternative method, metal oxide powder is mixed with organic foaming agents. These materials are typically two liquids which when mixed, react to evolve a foaming gas, and then cure to give a solidified foam with either an open or closed structure. The metal powder is mixed with one or both of the precursor liquids prior to production of the foam. The foam is then fired to remove the organic material, leaving ceramic foam. This is then electrolytically reduced.

#### Production of titanium or titanium alloy components

A near net shape titanium or titanium alloy component is made by electrolytically reducing a ceramic facsimile of the component made from a mixture of titanium oxide or a mixture of titanium oxide and the oxides of the appropriate alloying elements. The ceramic facsimile could be produced using any of the well known production methods for ceramic articles, including pressing, injection moulding,

extrusion and slip casting, followed by firing (sintering), as described before. Full density of the metallic component would be achieved by sintering, with or without the application of pressure, and either in the electrolytic cell, or in a subsequent operation. Shrinkage of the component during the conversion to metal or alloy would be allowed for by making the ceramic facsimile proportionally larger than the desired component.

This method would have the advantage of producing a component near to the final desired net shape, and would avoid costs associated with alternative shaping methods such as machining or forging. The method would be particularly applicable to small intricately shaped components.

## Claims

1. A method of removing oxygen from a solid metal, metal compound or semi-metal  $M_1O$  by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$  and wherein, the metal, metal compound or semi-metal is in the form of a granules.
2. A method as claimed in claim 1 wherein said granules are agitated.
3. A method of removing oxygen from a solid metal, metal compound or semi-metal  $M_1O$  by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$  and wherein, the metal, metal compound or semi-metal is in the form of a powder which is continuously fed into the fused salt.
4. A method of removing oxygen from a titanium dioxide by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$  and titanium dioxide is predominantly in the form of amorphous slurry with a quantity of between 5 and 95 percent calcined titanium dioxide
5. A method of producing a metal foam comprising the steps of fabricating a foam-like metal oxide preform, removing oxygen from said foam structured metal oxide preform by making the preform a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$ .
6. A method as claimed in claim 5 wherein said metal oxide preform is produced by infiltrating a polymeric foam with metal oxide slip which is then dried and fired.

7. A method as claimed in claim 5 wherein the metal oxide preform is produced by the steps of:
  - a) mixing the metal oxide powder with organic foaming agents so as to evolve a foaming gas;
  - b) curing to give a solidified foam; and,
  - c) firing the foam to remove the organic material.
8. A method as claimed in claim 6 wherein said metal oxide preform is sintered metal oxide granules.
9. A method of producing a metal matrix composite comprising:
  - a) blending particulate reinforcement with metal oxide powder to provide a mixture;
  - b) sintering said mixture; and
  - c) removing oxygen from sintered mixture by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$ .
10. A method of producing a fibre reinforced metal matrix composite comprising:
  - a) coating reinforcement fibres with a metal oxide/binder slurry to produce a pre-form; and
  - b) removing oxygen from the preform by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$ .
11. A method for producing titanium powder from titanium dioxide comprising the steps of; the providing titanium oxide as a first cathode;
  - a) removing oxygen from the titanium dioxide in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2$ ;
  - b) providing a second cathode maintained at a potential which is more negative than the first cathode such that dendritic titanium is deposited thereon; and
  - c) collecting the titanium deposited on said second cathode.

12. A method of producing a titanium or titanium alloy component comprising:
  - a) providing a ceramic facsimile of the component from titanium oxide or a mixture of titanium dioxide and oxides of appropriate alloying elements;
  - b) removing oxygen from facsimile by making it a cathode in a fused salt of  $M_2Y$  or a mixture of salts, which comprises conducting electrolysis under conditions such that ionisation of oxygen rather than  $M_2$  deposition occurs at an electrode surface and that oxygen dissolves in the electrolyte  $M_2Y$ .



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Application No: GB 0003971.9  
 Claims searched: 1-4

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Examiner: Pete Beddoe  
 Date of search: 16 November 2000

## Patents Act 1977

### Search Report under Section 17

#### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C7B (BDCA, BDCC, BDCF, BDCJ, BDCK, BDCN, BDDA, BDDA, BDDDB, BDDC, BEDL)

Int Cl (Ed.7): C22B (21/00, 21/02, 21/04, 34/12); C25C (3/26, 3/28); C25F (1/12, 1/16)

Other: Online: WPI, EPODOC, JAPIO

#### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X,A	WO 99/64638 A1 (CAMBRIDGE UNIVERSITY) see esp exs & fig 1	1-4
X	GB 781803 (HORIZONS) see esp exs	1-4
A	Nature, Vol 407, 21 September 2000, G Z Chen et al, "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride", pages 361-364, see whole article	1-4
X,A	Journal of Alloys and Compounds, Vol 237, 15 April 1996, D R Sadoway et al, "Electrochemical deoxidation of yttrium-oxygen solid solutions", pages 150-154, see esp "experimental" section	1-4
X,A	Metallurgical Transactions B, Vol 24B, June 1993, T H Okabe et al, Electrochemical Deoxidation of Titanium, pages 449-455, see esp "Experimental" and "Results" sections	1-4
X,A	Acta Chemica Scandinavica, Vol 45, 1991, S Boghosan et al, "Oxide Complexes in Alkali-Alkaline-Earth Chloride Melts, pages 145-157, see esp p146 lines 21-34 (LHS) & p150 et seq	1-4

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



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Application No: GB 0003971.9  
Claims searched: 5-8

Examiner: Pete Beddoe  
Date of search: 17 May 2001

## Patents Act 1977 Further Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.S): C7B (BCBX, BDCA, BDCC, BDCF, BDCJ, BDCK, BDCN, BDDA, BDDDB, BDDC, BEDL)  
Int Cl (Ed.7): C22B (21/00, 21/02, 21/04); C25C (3/00, 3/26, 3/28, 5/00, 5/02, 5/04); C25F (1/12, 1/16)  
Other: Online: WPI, EPODOC, JAPIO

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 781803 (HORIZONS) see esp ex II	5 at least
X	WO 99/64638 A1 (CAMBRIDGE UNIVERSITY) see esp p13 lines 15-22	5 at least
X	WO 98/49371 A1 (ALTA) see esp p9 line 30 - p10 line 12 & p10 line 25 - p11 line 9	5 at least
X	US 4187155 (DIAMOND) see esp exs 1,2,3	5 at least
A	Nature, Vol 407, 21 September 2000, G Z Chen et al, "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride", pages 361-364, see whole article and esp 2 <sup>nd</sup> para of "Methods" section at page 363	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.